

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.



Consommation
et Corporations Canada

Consumer and
Corporate Affairs Canada (21) (A1)

2,024,509

Bureau des brevets

Patent Office

(22)

1990/09/10

Ottawa, Canada
K1A 0C9

(43)

1992/02/04

(52)

167-302

5,018,7/06

(51) INTL.CL.⁵ A61K-7/09; A61K-7/13

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Dyeing and Perming Process

(72) Murphy, Bryan P. - U.S.A. ;

(73) Bristol-Myers Squibb Company - U.S.A. ;

(30) (US) 562,530 1990/08/03

(57) 14 Claims

Notice: The specification contained herein as filed

Canada

CCA 3254 (10-89) 41

BACKGROUND

The use of isothiuronium dyes to color various fibers, including hair, has been reported by Guise and Stapleton in the Journal of the Society of Dyers and Colorists at 91, pp. 259-264. In the Guise et al article, hair is dyed, with and without hydrogen peroxide and fixed with an ammonia wash. Thus, the use of the isothiuronium colorants in two (ie., dye, then wash) or three (ie., treat with peroxide, dye, then wash) steps has been described in the prior art.

The use of colorants in the second, or oxidizing, step of a two-step process for dyeing and perming hair at the same time is described in U.S. 4,630,621 to Pontani. The Pontani system uses a first reducing step to break the disulfide linkages in the untreated hair and then uses an oxidizing step to rebound the disulfide linkages. Pontani adds colorants after the reducing step so that, via the second step, the hair is permed (ie., bound into a new configuration) and colored (via the action of the colorant) at the same time.

Other publications which deal with isothiuronium or related molecules and their use to color fibers are:

U.S. 3,534,135 describes the use of dithioureas or N-alkyl dithioureas in setting compositions to be used on hair in which the disulfide linkages have been broken to help restore disulfide linkages.

U.S. 3,803,323 shows compositions containing aminoalkylisothiuronium compounds, which compositions help minimize excessive oiliness in the hair and scalp.

U.S. 3,966,928 and 4,041,033 deal with the use of 3-(2-oxopyridazinyl)isothiuronium compounds as antimicrobial agents in shampoos and hair dressings.

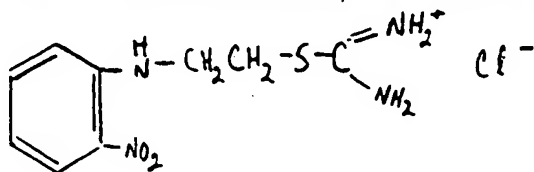
Guise et al, "New Approaches to Washfast Dyes for Wool: I. Isothiuronium Salts as Protected Reactive Groups", Journal of the Society of Dyes and Colorists, (July, 1978), pp. 223-8.

This publication deals with the stability of isothiuronium salts to hydrolysis depending upon the N-substituent. No recitation of hair dyeing is found therein.

The Invention

It has been found that hair can be colored with isothiuronium dyes in the initial, or reducing, step of a 2-step reduction/oxidation perming operation or immediately afterwards, but before rebonding (oxidation).

In a preferred embodiment, the dye of formula I,



(I)

is applied along with thioglycollate to untreated hair and then treated with peroxide. The hair was dyed a yellow color.

Following six shampoos with a conventional shampoo, the change in Hunter Tristimulus values, as measured by the calculation $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$, is only 0.21. Thus, the washfastness of these colorants, when applied along with the reducing reagent in a reduction/oxidation perming system, is excellent.

Advantages of the Invention

The invention has several advantages over other methods for coloring and perming hair.

Firstly, the dyeing composition is easy to formulate, since it contains only conventional reducing agent(s) and isothiuronium salt(s).

Next, the application of the dye is less complex than some other, eg., oxidative, dyeing systems. The hair need not be pretreated with metal catalysts and/or pH modifiers before the colorant is applied.

In addition, the peroxide reagent which is applied after the reducing step is a conventional oxidizer. Thus, the need for costly oxidizers (ie., reforming agents) is eliminated.

The formulation of the dye/reducing agent combination requires only simple mixing. The high solubility of isothiuronium salts in aqueous systems, with or without alcohol solvents, assures this ease of mixing.

Lastly, because the color-forming reaction takes place at the same time that the disulfide links are being broken, the likelihood of causing damage to the hair--eg., dryness, brittleness, breakage--is minimized. In many dyeing/perm systems, the pre-treatment of the hair with a reducing agent weakens the hair shaft by increasing its porosity.

These and other advantages will be apparent after a consideration of the following description and claims.

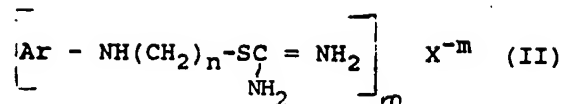
Description of the Invention

Unless otherwise stated, all percentages recited are weight percentages based on total composition weight.

The invention deals with compositions for both dyeing and perming (preferably reducing) hair in one step, as well as with a two-step sequence in which the perming and coloring step is followed by an oxidation step. The compositions used in the dyeing and perming step contain one or more isothiuronium dyes and one or more reducing agents.

Isothiuronium Salts

The isothiuronium salts which are useful in the invention are salts of formula II:



wherein:

Ar is an aromatic moiety having up to five non-isothiuronium substituents, n is an integer from 1 to 5, and X is any suitable leaving group, preferably an anion selected from the group consisting RSO₃, of SO₄ Cl, Br, I, and F. X is more preferably a monovalent Br, I or RSO₃ group

R is a residue of toluene, benzene or methane. R is preferably toluyl or methyl. Methyl is highly preferred.

"m" is generally 1 or 2, but preferably 1.

Useful Ar groups include substituted and unsubstituted phenyl, diphenyl, arylmethane, naphthyl, indole, anthiaquinone and naphthaquinone residues containing from 6 to 24 carbon atoms. Phenyl substituted phenyl anthraquinone and substituted anthaquinone groups are preferred. Nitrophenyl, hydroxynitrophenyl, aminonitrophenyl and methylaminanthraquinone residues are highly preferred.

The substituents on the Ar group may be any of a variety of groups commonly found in dye molecules. Thus, Cl, Br, I, F, NO₂, NH₂, NR¹R², OR¹, SR¹, CN, CF₃, C(O)NR¹R² and the like may be substituents. Generally, from 1 to 4 substituents will be on each ring of the Ar group.

R¹ and R² may be independently be H, C₁₋₆ alkyl, or C₁₋₆ mono- or polyhydroxy-alkyl. Alkyl groups bearing one or more of the substituents set out above are operable.

Mixtures of dyes are operable.

The number "n" can be any value from about 1 to about 5, with about 2 to about 4 preferred, and 2 or 3 highly preferred. The X moiety in formula II, can be any halide group. However, it is preferred that X be a Cl or Br group.

The dyes of the invention are prepared by the process set out in the Journal of the Society of Dyers and Colorists, at 91, pp. 259-264.

The use of other conventional dyes, as well as couplers and/or dye assistants, in suitable amounts is contemplated.

Reducing Agents

The reducing, or reforming, agents used in the conjoint relaxing and dyeing step are conventional.

Generally, the reductants are thioglycollic acid derivatives, such as sodium thioglycollate, ammonium thioglycollate, potassium thioglycollate, glycerol monothioglycollate, and the like. Mixtures are operable.

In addition, other reducing agents which are conventionally used in relaxing hair can be used. These include bisulfites, and the like. Mixtures can be used.

Dye/Reducing Agent Combinations

The dye and reducing agent are combined at dye/reducing agent ratios of about 1:100 to about 3:1, preferably about 1:20 to about 1:3, based upon weight proportions.

Generally, the dye and reducing agent are combined in an aqueous medium, which may, optionally, contain cosolvents, such as ethanol, ethylene glycol monomethyl ether, isopropanol, benzyl alcohol, and the like.

When diluents are present, they are used in quantities of from about 0.1 to about 20 wt. %.

The combination, or mixture, of the dye and reducing agent may be applied via conventional methods eg., spraying, brushing, rinsing, etc. when it is of appropriate consistency, eg., liquid.

When a thickened composition, eg., a gel or paste, is used, the application of the colorants may involve simple spreading or may include the use of foams or other more thixotropic forms.

When a foamable composition is desired, the presence of suitable amounts of one or more foaming agents is contemplated.

It is preferred that the dye/reducing agent combination have a pH of between about 4 and about 11, preferably about 5 to about 10 depending upon the reductant used. Buffers may be used.

Oxidation Agents

The second, or oxidation, step of the dyeing and perming or relaxing process--ie., the oxidation portion of the reduction/oxidation sequence--uses conventional oxidizing agents or oxidizers.

Useful oxidizers include: peroxides, bromates, and the like. Mixtures are operable.

One preferred oxidizer or rebonding agent is hydrogen peroxide. Its use, with or without other oxidizers, is contemplated.

The oxidizing component is generally applied via an aqueous composition. When solutions in water or other conventional diluents are used, they usually contain from about 0.25 to about 4.5 wt. % of the oxidizer.

The oxidation agents, like the dye/reducing combinations, can be applied in various liquid and/or more thioxotropic forms, as well as via foams, gels, pastes and the like. The various additives discussed above may be used, in suitable quantities, in the oxidation agents.

When a peroxide oxidant is employed, one or more subsequent applications may be made to the hair in order to lighten the final color thereof.

The Total Coloring and Perming System

In general, the dyeing and perming system of the invention involves two essential steps:

(1) contacting the hair with the combination of dye and reducing agent, and

(2) subsequently, contacting the hair with an oxidizing agent (ie., an oxidizing composition).

The Total Coloring and Perming System

It is recommended that the hair be rinsed between steps (1) and (2) to stop the reaction and to minimize the risk of damage to the hair or skin. If desired, the reducing agent can be applied immediately before, in combination with, or after the dye in a separate step. It is a requirement of the invention that at least part of the isothiuronium salt used be applied to the hair before the final oxidizer is applied thereto.

The use of additional treatment(s) with oxidizing agent is contemplated. It should be noted that hydrogen peroxide can also function as a color modulator or lightener after the initial coloring operation is complete.

While they are not required, the use of supplemental agents, eg. primary intermediates, couplers, auxiliary colorants and the like, is contemplated. When used, they will be present in amounts of about 10% or less.

The dyeouts obtained using the coloring system of the invention are permanent, ie., do not wash out within ten shampoos, and are stable to subsequent processing of the hair. Accordingly, normal operations such as styling, blow drying, drying, hot curling, etc. can be carried out subsequent to the reducing and oxidizing steps without damaging the hair.

Application Times

The amount of time needed for each of the two essential steps varies with the nature of the relaxing system. Conventionally, the reducing step--or, in this case, the reducing and dyeing step--takes from about 10 to about 60 minutes, preferably about 15 to about 30 minutes.

Following a water rinse to remove the excess reducing agent and excess colorant, the oxidizing composition is applied. Generally, the oxidation step will take from about 5 to about 30 minutes. While a simple rinse with oxidizer is operable, it is desirable that the oxidizer be applied as part of a shampoo composition and/or a conditioning composition. When applied via shampoo, 2 to 3 latherings are generally sufficient to ensure enough time for reaction.

When a conditioner is used as the vehicle for the oxidizer, it should be contacted with the hair for about 2 to about 20 minutes, preferably 5 to 15 minutes, to insure proper reaction.

Following the oxidation step, a water rinse is used to remove the reagent(s).

The dyeings obtained, while permanent, are removable to some extent. The use of reducing agents to effect reversal of the reaction is contemplated. The coloring and perming system described herein is adaptable for use as a kit. When a two-part kit is used, one container will house the reducing (perm) agent along with the dye, while the other will house the oxidizer. Alternatively, a three-part kit is usable. In such a kit, the reducing (perm) agent will be in one container, the dye in a second and the oxidizer in a third. The use of

kit, the reducing (p rming) agent will be in one container, the dye in a second and the oxidizer in a third. The use of a three-part kit may entail (a) premixing the contents of the first and second containers, or (b) applying their contents separately.

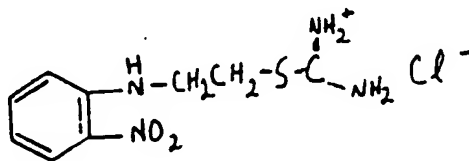
Substrates

While this description refers to the treatment of hair on a living human head, it should be noted that the kits, compositions and processes described may be used on other substrates as well. For instance, non-living hair, eg., wigs, doll's hair, fur and the like, can also be treated using this system. In general, any fibrous keratinaceous substrate can be treated.

Examples

The following examples illustrate the invention.

The compound I is:



Examples 1 and 2 show use of the coloring system with reducing agents. Examples 3-5 show coloring in the absence of a separate application of reducing agent.

EXAMPLE 1

A two gram blended gray hair swatch is treated with four grams of a reducing solution (e.g. 6% ammonium thioglycollate at pH 9.2) for twenty

minutes, then rinsed under tap water for two minutes. A 1% solution of compound I in water is applied to the hair. After twenty minutes, the hair is rinsed, and five grams of a 6% H_2O_2 solution is applied to the hair, and left for ten minutes.

The hair is rinsed and blown dry to give a bright yellow color that has increased resistance to shampooing.

EXAMPLE 2

A two gram blended gray hair swatch is treated with compound I dissolved in a reducing solution (e.g. 1% dye in a 6% ammonium thioglycollate solution at pH 9.2) for twenty minutes, then rinsed under tap water. Five grams of a 6% H_2O_2 solution is applied, and left for twenty minutes.

The hair is rinsed and blown dry to give a shampoo resistant, bright yellow swatch.

EXAMPLE 3

A two gram blended gray hair swatch is treated with compound I dissolved water (pH 5). After twenty minutes, the bath is raised to pH 11, and left for another ten minutes. Five grams of 6% H_2O_2 is added to the alkaline bath and left for ten minutes.

The hair is rinsed and blown dry to give a bright yellow swatch that has increased resistance to shampooing.

EXAMPLE 4

Compound I is hydrolyzed to the free thiol with aqueous KOH, the solution is adjusted to pH 10, and a two gram blended gray hair swatch is treated with this solution for thirty minutes. Five grams of 6% H_2O_2 is added to the alkaline bath and left for ten minutes.

The hair is rinsed and blown dry to give a bright yellow swatch that has increased resistance to shampooing.

EXAMPLE 5

In an application similar to example 4, compound I is hydrolyzed to the free thiol with aqueous KOH, the solution is adjusted to pH 10, and a two gram blended gray hair swatch is treated with this solution for thirty minutes. The hair is rinsed with tap water, and then treated with five grams of 6% H_2O_2 for ten minutes.

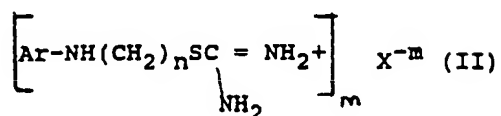
The hair is rinsed and blown dry to give a shampoo resistant, bright yellow color.

Thus, the invention pertains to a system which may be used for simultaneously or concurrently dyeing and perming hair via the use of a isothiuronium colorant in or after a reducing step, followed by an oxidizing step.

Reasonable variations, such as those which would occur to a skilled artisan, can be made herein without departing from the scope of the invention.

What is claimed is:

1. A composition useful for perming hair while coloring it comprising:
 - (a) a reducing agent, and
 - (b) a compound of formula II



wherein:

Ar is an aromatic moiety bearing up to five non-isothiuronium substituents,

n is an integer from about 1 to about 5,

m is 1 or 2, and

X is a suitable leaving group.

2. The composition of claim 1 wherein the reducing agent is a thioglycollic acid or a derivative thereof.

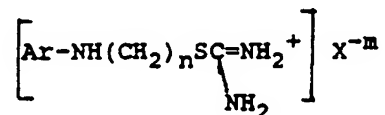
3. The composition of claim 2 wherein the reducing agent is sodium or potassium thioglycollate.

4. The composition of claim 2 wherein Ar is a phenyl group, n is 2 to 4, and X is Cl or Br.

5. The composition of claim 2 wherein Ar is nitrophenyl, n is 2 and X is Cl.

6. A process for the simultaneous perming of hair while coloring it comprising the steps of:

(1) contacting the hair with the a composition containing a reducing agent and a compound of formula II



wherein

Ar is an aromatic moiety bearing up to five non-isothiuronium substituents,

n is an integer from about 1 to about 5,

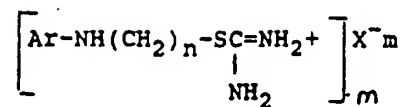
m is 1 or 2, and

X is a suitable leaving group; and

(2) subsequently contacting the hair with an oxidizing composition.

7. The process of claim 6 wherein the reducing agent is a thioglycollic acid or a derivative thereof.
8. The process of claim 7 wherein the reducing agent is sodium or potassium thioglycollate.
9. The process of claim 7 wherein Ar is a phenyl group, n is 2 to 4 and X is Cl or Br.
10. The process of claim 9 wherein Ar is nitrophenyl, n is 2 and X is Cl.
11. The process of claim 10 wherein the oxidizing composition contains a peroxide.
12. A kit for treating hair to dye and perm or relax it concurrently comprising:
 - (a) in a first package, a combination of a reducing agent and an isothiuronium dye,
 - (b) in a second package, an oxidizing agent.
13. The kit of claim 12 wherein (a) contains a thioglycollic acid or derivative.

14. The kit of claim 13 wherein (a) contains a dye of formula II:



II

wherein

Ar is an aromatic moiety bearing up to five non-isothiuronium substituents,

n is an integer from about 1 to about 5,

m is 1 or 2, and

X is a suitable leaving group.